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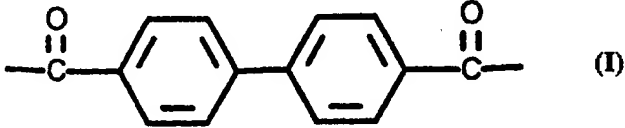
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : B32B 27/06</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/13478 (43) International Publication Date: 23 June 1994 (23.06.94)</p>
<p>(21) International Application Number: PCT/US92/10707 (22) International Filing Date: 9 December 1992 (09.12.92)</p> <p>(71) Applicants (for all designated States except US): HOECHST AKTIENGESELLSCHAFT [DE/DE]; Postfach 800 320, D-6320 Frankfurt am Main 80 (DE). HOECHST CELANESE CORPORATION [US/US]; Route 202-206 North, Somerville, NJ 08876 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): BENNETT, Cynthia [US/DE]; Mainstrasse 22, D-6200 Wiesbaden (DE). CHOE, E-Won [US/US]; 130 Radtke Road, Randolph, NJ 07869 (US). FLINT, John, Anthony [GB/US]; 150 Lenape Lane, Berkeley Heights, NJ 07922 (US). KUHMAN, Bodo [DE/DE]; Lindenstrasse 5, D-6258 Runkel 5 (DE).</p> <p>(74) Agents: CLEMENTS, Gregory, N. et al.; Hoechst Celanese Corporation, 4000 Barclay Downs Drive, Patent Department, Charlotte, NC 28232-2414 (US).</p>		<p>(81) Designated States: CA, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report.</p>
<p>(54) Title: BIAXIALLY ORIENTED PENBB FILM FOR GLAZING, OPTICAL AND WEATHERABLE APPLICATIONS</p> <p>(57) Abstract</p> <p>Disclosed herein is a mono- or multilayered, biaxially oriented film, wherein at least one layer essentially consists of PENBB and wherein at least one surface of the film is coated with an adhesive and/or optically active layer. This film has many advantages, including UV radiation stability, strength, transparency and low color, making it useful in optical, glazing and weathering applications. PENBB as disclosed herein is a copolyester containing units of formula (I).</p> <div style="text-align: center;">  <p>(I)</p> </div>		

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BIAXIALLY ORIENTED PENBB FILM FOR GLAZING, OPTICAL AND WEATHERABLE APPLICATIONS

Background Of The Invention

5 Polymeric films are used extensively in applications where the film is exposed to intense electromagnetic radiation, particularly in the infra-red, visible, and ultraviolet range. In some cases the film is used to transmit such radiation, while in others the film may be a substrate for coatings designed to reflect bands of incident radiation.

10 One common film material, polyethylene terephthalate (PET), has excellent mechanical strength and clarity, but tends to degrade due to radiation absorption in the ultraviolet range. Thus, when this film is exposed for long periods to direct sunlight, it degrades and becomes useless. Under some conditions, such degradation may occur after only a few months of exposure.

15 Some radiation protection can be obtained by addition of ultraviolet stabilizers. However, such stabilizers may induce color formation in the film that makes the product less desirable for certain applications. Another problem with such additives is that they tend to be unstable under conditions present during film extrusion. This results in loss of effectiveness and forming of hazardous vapors. Some stabilizers may exude from the crystalline polymer film during further processing.

20 On the other hand, some inherently UV stable polymers are known, for example fully aromatic polyesters such as the copolyester of bisphenol A with isophthalic and terephthalic acid or the copolyester of p-hydroxybenzoic acid with 2-hydroxy-6-naphthalic acid. Unfortunately, films of such polymers are either mechanically weak and subject to chemical attack when amorphous or are opaque when "liquid crystalline".

25 U.S. Patent No. 3,008,934 discloses copolyesters containing as acid derived units 4,4'-bibenzoate and a host of other dicarboxylates including 2,6-naphthalic dicarboxylate. It also discloses oriented fibers and films prepared from these copolyesters, however, biaxially oriented PENBB films are not

disclosed or envisioned. In particular, those films with improved stiffness (tensile modulus) and tensile strength in both MD and TD as well as thermostability, UV stability, hydrophobicity, dimensional stability and impermeability toward gases in comparison to PET film are not disclosed in

5 U.S. Patent No. 3,008,934.

An inherently UV resistant film with mechanical properties similar to PET film would offer real advantage to such markets as architectural and automotive glazing, solar collection devices, solar control devices, sign constructions, architectural fabric laminates, and the like. Colorless, highly

10 transparent, stiff and strong and flexible film with extended life in high intensity solar environments are required.

Where the optical end-uses for plastic films utilize the film as the base for optically active coatings, the need is for high strength combined with selective optical effects. Reflective coatings may be applied which reflect

15 infrared light, but have little or no effect on ultraviolet or invisible radiation.

Scope Of The Invention

The present invention provides a biaxially oriented polymeric film containing at least one layer of PENBB copolyester resin with excellent optical

20 properties and ultraviolet light resistance, and optical, glazing, and weatherable products made therefrom.

Description Of The Invention

Copolyesters of PENBB can be processed into film and sheet using

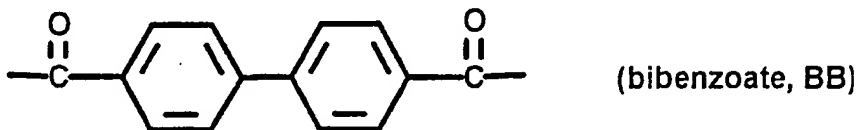
25 processing equipment similar to that used for polyethylene terephthalate sheet to give clear transparent biaxially oriented film.

PENBB as mentioned herein is a copolyester containing acid-derived units of which at least 25 mole percent are bibenzoate units. The remainder of the acid-derived units are difunctional units such as 2,6-dicarboxy

30 naphthalate, terephthalate, isophthalate, 5-sodium sulfoisophthalate, adipic acid or poly functional units such as trimellitic acid, pyromellitic acid, and p-hydroxy benzoic acid. The diol units of the copolyester may be chosen from

ethylene glycol, diethylene glycol, propylene glycol, neopentyl glycol, 1,4 cyclohexane dimethanol, and p-xylene glycol.

The preferred PENBB copolyester film contains 40 - 60 mole percent of 4,4'-bibenzoate (BB)



and 60 - 40 percent of 2,6-dinaphthalate (N) as the acidic reactors in the polymer and at least 80 mole percent ethylene glycol (E) as the diol component.

10 The copolyester is obtained by polycondensation of the corresponding diacid or lower dialkyl diester and the corresponding diol. Both components should normally be employed in equimolar ratios. It may, however, be advantageous to employ one of the components -- especially the diol -- in excess, for instance in order to influence the reaction kinetics or to serve as a solvent. The polycondensation is carried out according to known processes used, e.g., in the production of polyethylene terephthalate (PET). Usually
15 about 100 mole percent of the dicarboxylic acid or dialkyldicarboxylate or a corresponding mixture of two or more of these acids and/or esters are mixed with > 100 mole percent of the corresponding diol(s). This mixture is then heated to about 200°C, preferably in the presence of a transesterification catalyst, until sufficient lower alkyl alcohol has been removed from the
20 mixture via distillation. This reaction yields an oligomer or a low molecular weight polyester, which is subsequently subjected to polycondensation, preferably in the presence of a stabilizer and/or catalyst. Useful stabilizers and catalysts can be polyphosphates, triorganyl phosphates, antimony trioxide or tetraalkoxy titanate(IV) or mixtures of triphenylphosphate and antimony
25 trioxide. A preferred process for the production of such copolyesters is described in U.S. Patent Application Serial No. 07/735,553 which is incorporated herein by reference. A further increase in molecular weight can

be achieved by solid phase polycondensation at a temperature just below the melting point, under vacuum, or in a stream of dry air or inert gas.

In order to achieve the desired mechanical properties in the biaxially oriented PENBB film it is recommended that the IV value (inherent viscosity, as measured in a 1 : 1 weight-ratio mixture of pentafluorophenol and hexafluoroisopropanol at a concentration of 0.2 g/dl and a temperature of 25 °C) of the PENBB polymer after extrusion be > 0.5 dl/g and preferably > 0.55 dl/g.

To produce the film, the polymer melt is extruded through a die onto a chill roll where it solidifies, is then biaxially oriented, heat set, optionally post treated, and then wound on a roll. The solidified film as extruded on the chill roll should be obtained in a mainly amorphous state. To achieve this, the melt film must be pinned to the chill roll by a known method such as electrostatic pinning or vacuum, air knife or the like.

The biaxial orientation of the film is achieved by stretching the film at elevated temperature in the machine direction (MD) and transverse direction (TD). This stretching can be either simultaneous or sequential. In the case of sequential stretching the first stretching step can be in either MD or TD, followed by stretching in the other direction. The orientation in MD can also be achieved in several steps, either one after another prior to stretching in TD, or before and after the TD stretching. Preferred temperatures for stretching lie between the glass transition temperature and about 30 °C above the cold crystallization temperature of the PENBB copolymer composition in use (both temperatures can easily be measured on amorphous films by DSC). Suitable total stretch ratios in MD and TD lie between 1 to 2 and 1 to 10, preferably between 1 to 2.5 and 1 to 5. The product of the MD and TD total stretch ratios should be between 1 to 30 preferably between 5 to 20. Biaxial drawing is performed such that the birefringence is < 0.2, preferably < 0.1 to ensure adequate isotropic properties. For some optical applications, it may be preferable to biaxially orient the film such that the birefringence is close to 0. Birefringence as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the

film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

In order to optimize properties such as shrinkage, relaxation steps can be included in the orientation and heat setting processes.

5 The heat setting takes place at a temperature between the cold crystallization temperature and the melt temperature of the copolymer composition.

In some cases a surface treatment such as corona, plasma or flame treatment should be employed before winding the film on a roll.

10 It has been found that PENBB film has excellent UV stability. Thin cross-sections of the PENBB polymer, as well as polyethylene terephthalate (PET) and polyethylene naphthalate (PEN), were exposed to ultraviolet light radiation in a UV weathering tester (QUV weatherometer) wherein the samples were alternately exposed to 4 hours of UV radiation and 4 hours of
15 moisture. Samples were removed at 1, 2, 5, 10 and 20 day intervals and then tested for tensile properties. After 20 days the PENBB samples retained 96 percent of their break strength. The polyethylene terephthalate samples had lost 94 percent of their strength in the same test. The PEN samples showed 20 percent loss in the same period. It has been demonstrated by I.
20 Ouchi et al (J. Applied Polymer Science (1976), Vol. 20, p. 1983) that PEN has substantially better outdoor life than PET indicating the relationship between laboratory data and outdoor environmental effects. Thus, based on the laboratory data, the PENBB film would be expected to have greater retention of properties when exposed to outdoor environments for extended
25 periods of time.

Films according to the present invention have an excellent combination of properties, including transparency, UV radiation stability, strength, and colorlessness. Such films are well suited for optical, glazing, and weathering applications.

30 The PENBB copolyester film may be produced in a single layer, or in multilayers by well known techniques, such as coextrusion. When multilayer film is produced, each layer may be the same PENBB copolyester composition

or formulation. More likely, each layer of the PENBB copolyester would vary in formulation. In a preferred case, one layer of a two layer coextrusion is substantially thinner than the other layer, and said layers contain particulate matter designed to improve slip characteristics of the film. The size, distribution and concentration of the particulate would be sufficient to achieve desirable slip properties without negatively impacting the excellent optical transparency or brilliance of the film structure.

A similar embodiment is a three layer coextrusion wherein both outer layers would be a PENBB copolyester formulation that contains the particulate matter. Such outer layers are each 10 percent or less of the total film thickness.

A further embodiment of the coextrusion concept includes the use of other polymers or copolymers as alternative layers. Thus the use of polyethylene terephthalate, polyethylene isophthalate, or copolyesters containing these polyesters plus 2,6-dinaphthoic acid, p-hydroxybenzoic acid, etc., may be used. Such materials may also contain slip control agents or other additives.

The PENBB copolyester film or coextruded films containing the PENBB copolyester may subsequently have coatings or surface depositions made thereon, designed to optimize optical performance of the film. Typical coatings or depositions may include silver, gold, aluminum, or other vacuum deposited metals or combinations of metals, metallic oxides, metallic nitrides, silica deposits, carbon (amorphous or crystalline), organic polymers, optically or electrically active liquid crystalline materials, such as used in "Liquid Crystal Displays" (LCDs), and the like.

Such coatings or depositions may be designed to selectively absorb, transmit, or reflect portions of the electromagnetic spectrum. Such coatings may, for example, selectively reflect infrared radiation and be useful for window constructions used to control interior building temperatures. Other such coatings may selectively absorb infrared radiation for solar energy devices. Such coatings may also reduce UV transmission, thus increasing performance life of the substrate film.

These coatings may be applied by conventional coating techniques or by vacuum deposition techniques, such as resistance heated vacuum deposition, induction heated vacuum deposition, sputtering, reactive plasma deposition, and the like.

- 5 A further substantial advantage of uncoated film products produced from PENBB copolyesters is their excellent optical transmission and brilliance. These properties are especially important for automotive and architectural glazing applications.

10

EXAMPLE 1

- 289 parts by weight of dimethyl 2,6-naphthalenedicarboxylate, 322 parts by weight of dimethyl 4,4'-bibenzoate, 368 parts by weight of ethylene glycol and 0.7 parts of manganese acetate tetrahydrate were initially introduced into a conventional polycondensation reactor provided with a
15 blanketing gas line (N₂), pressure equalization, a thermometer, a condenser, a vacuum connection and a stirrer. The mixture was heated at 220°C for 2.5 hours, during which time methanol was distilled off. 0.675 parts by weight of triphenyl phosphate and 0.2259 parts of antimony trioxide were then added as polycondensation catalysts and the mixture was heated to 270°C,
20 with stirring. Vacuum was applied and the temperature was raised to 285°C and maintained for 2.5 hours. A portion of the copolyester thus obtained was ejected from the reactor in the form of melt under nitrogen pressure and solidified as a thin, clear, amorphous film. A glass transition temperature (T_g) of 123°C and a cold crystallization temperature (T_{cc}) of 132°C was
25 determined for the film by means of DSC.

The residual melt was granulated. The granules were white, opaque and crystalline. An IV value of 0.56 dl/g was determined for the granules (measured at a concentration of 0.1 g/ml in pentafluorophenol/hexafluoroisopropanol (weight ratio 1:1) at 25°C).

30

The granules were further condensed for 20 hours at 240°C under vacuum in the solid phase. After this treatment the IV value was 1.1 dl/g. As expected, no T_g or T_{cc} was discernable in the DSC recording for the

crystalline granules condensed in the solid phase; the melting point (T_m) was 281°C.

The PENBB granules having a melting point of 281°C were melted in a single screw extruder at temperatures of 280 to 320°C and extruded through a sheet die onto a cooling roll temperature controlled at 30°C. A 120 μ m thick pre-film was obtained which was clear and transparent. Its density was 1.312 g/cm³.

The PENBB pre-film was sequentially biaxially oriented (first transversely then longitudinally: 3.5 x 3.5) at 140°C on a film stretching device. An 8 μ m thick, clear film was obtained. The film was clamped in a tenter frame and heat treated at 260°C for 10 minutes. Its density was 1.343 g/cm³. The mechanical properties were:

	Longitudinal	Transverse
Modulus of Elasticity:	9.2 GPa	8.0 GPa
15 Tear Strength:	237 MPa	182 MPa
Transparency	87 Percent (Hazegard System)	

THAT WHICH IS CLAIMED IS:

1. A mono- or multilayered, biaxially oriented film, wherein at least one layer essentially consists of PENBB and wherein at least one surface of the film is coated with an adhesive and/or optically active layer.
5
2. A mono- or multilayered, biaxially oriented film according to Claim 1, wherein the PENBB layer(s) have a birefringence less than 0.2 and an wherein the IV-value of the PENBB is greater than 0.5 dl/g.
10
3. A mono- or multilayered, biaxially oriented film according to Claim 1 or 2, wherein both surfaces of the film are coated.
4. A mono- or multilayered, biaxially oriented film according to Claim 3,
15 wherein the coating on one surface of the film is an adhesive coating and the coating on the other surface of the film is an optically active coating.
5. A mono- or multilayered, biaxially oriented film according to Claims 1 to 3 wherein an adhesive coating and an optically active coating is applied.
20
6. A mono- or multilayered, biaxially oriented film according to Claims 1 to 3 wherein the optically active layer is a first layer on a surface of the film and the adhesive layer is a second layer on said surface of the film, wherein the second layer is applied on the first layer.
25
7. A mono- or multilayered, biaxially oriented film according to Claims 1 to 3 wherein the optically active layer is a first layer on one surface of the film and the adhesive layer is a second layer on said surface of the film, wherein the second layer is applied on the first layer and wherein an adhesive layer is
30 on the other surface of the film.

8. A mono- or multilayered, biaxially oriented film according to any one or more of Claims 1 to 7, wherein said adhesive layer comprises polyvinyl butyrate.

5 9. A mono- or multilayered, biaxially oriented film according to any one or more of Claim 1 to 8, wherein said optically active layer reflects a substantial amount of the electromagnetic radiation in at least one portion of the electromagnetic spectrum.

10 10. A mono- or multilayered, biaxially oriented film according to Claim 9, wherein said optically active layer comprises liquid crystals whose orientation vary by the application of heat and/or electricity.

15 11. Use of a film according to any one or more of Claims 1 to 10, as a protective layer.

12. Use of a film according to any one or more of Claims 1 to 10, as a protective layer in or for photovoltaic devices.

20 13. Glass, characterized in that a film according to Claims 1 to 10 is laminated thereon.

14. Fabric, characterized in that a film according to Claims 1 to 10 is laminated thereon.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10707**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) :B32B 27/06

US CL :428/910, 480, 343, 524

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/910, 480, 343, 524

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,716,061 (WINTER) 29 DECEMBER 1987. See Abstract.	1-4
A	US, A, 3,991,013 (PLETCHER) 09 NOVEMBER 1976. See Abstract.	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search

04 APRIL 1993

Date of mailing of the international search report

24 JUN 1993

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/10707

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.: 11-12
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Claims 11-12 are directed to a "use" PCT Article 17(2)(a)(i) "Use" claims not in a method terminology are not searched by this authority.

3. ☒ Claims Nos.: 5-14
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.